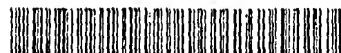


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- Hayes, John William  
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- Patch, Michael Ian  
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(54) Method of coating materials with a zeolite-type substance

(57) A substantially complete coating of a zeolite on-  
to a material such as catalyst particles can be achieved  
by treating the material prior to or simultaneously with

zeolite formation, with a polyelectrolyte. Copper catalyst  
systems show good hydrogen storage whilst blocking  
access of hydrocarbons to the catalyst.

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in the deposition of the zeolite, it may be desirable to assist agglomeration of the zeolite by admixing a non-miscible organic solvent, in order to deposit a thicker coating.

According to the particular application of the zeolite-coated product, other zeolites may be used, and, for example, the AVSi ratio may be adjusted for particular uses. Included within the term "zeolite" is that material known as silicalite. The zeolite may be modified *in situ* by ion exchange with a Group I metal, for example potassium ions may be exchanged for sodium ions in order to alter a Na-4A zeolite to a K-3A zeolite. Such 3A zeolites may offer improved performance and improved lifetime in the uses of present interest to the Applicants. Rubidium ions may also be used, and RbBr appears to offer a zeolite coating with improved stability in cycling processes.

Desirably, after formation of the zeolite-coated product, the product is calcined, eg at temperatures about 500°C, until the product is stabilised and shows no residual carbon (for example by microprobe) analysis.

The present invention is illustrated by the following examples which are not to be regarded as limiting the present invention in any way.

#### EXAMPLE 1

##### Preparation of Zeolite 4A-Coated Cu/Silica Hydrogen Storage Material

Cu(II) acetate (6.29g) was dissolved in a dilute solution of ammonia. The resulting copper solution was impregnated onto silica (20g) (3mm spheres, Norton, USA) with gentle heating. The material was dried at 100°C then calcined at 500°C to produce 10% Cu (oxide) on silica.

Pre-treatment was effected by adding the Cu/silica spheres (5g) to an aqueous alkaline solution (dilute ammonia) of 4wt% Percol 1697 (Allied Colloids Ltd) polyelectrolyte. The sample was then washed in dilute ammonia.

A zeolite gel was prepared by adding a solution of sodium metasilicate (15.51g in 52ml H<sub>2</sub>O) to a rapidly stirred solution of sodium aluminate (6.07g in 52ml H<sub>2</sub>O). The polyelectrolyte-coated spheres were added to the gel, and this mixture was agitated for 2 hours. The mixture was then transferred to a PTFE-lined autoclave bomb. The bomb was sealed then heated to 100°C for 24 hours. The bomb was then cooled to room temperature, opened and the contents washed with dilute ammonia to remove excess zeolite. The spheres were dried in an oven at 120°C, and finally calcined at 500°C for 2 hours.

##### Testing of Coated Hydrogen Storage Material

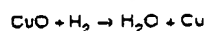
To test the hydrogen storage capacity of the coated

Cu/SiO<sub>2</sub>.

A 1g sample of the material was placed in a quartz reactor tube then oxidised by heating in flowing air to 500°C. The sample was then purged with N<sub>2</sub>. At a reactor temperature of 500°C, a gas mixture of 5% hydrogen in helium was passed over the sample; the composition of the outlet of the reactor was monitored by use of a mass spectrometer. The 1g sample was shown to remove 20ml of hydrogen.

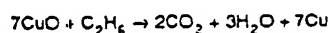
The sample was re-oxidised in flowing air then purged with nitrogen. At a reactor temperature of 500°C, ethane was then passed over the sample for 3 minutes at a flow rate of 40ml/min. The gas from the outlet of the reactor was collected; analysis by gas chromatograph showed that 0.85ml of CO<sub>2</sub> had been produced.

Assuming the following reaction:



one oxygen atom is used for every hydrogen molecule removed.

Assuming the following reaction:



then 3.5 oxygen atoms are used for every CO<sub>2</sub> molecule produced.

Thus, with the zeolite coating, 6.7 times more CuO was accessible by hydrogen than by ethane.

#### EXAMPLE 2

##### Preparation of a Zeolite 3A-Coated Cu/Silica Hydrogen Storage Material

The zeolite 4A-coated material prepared in Example 1 (5g) was immersed in a mobile solution of potassium chloride (2M in 500ml) for 48 hours. The material was then thoroughly washed with water to remove the excess salt, dried at 120°C, and calcined at 500°C for 2 hours. Electron microprobe analysis (TEM) of the samples showed that ~50% of the sodium cations that exist in the 4A coating have been exchanged by the larger potassium cations.

When the coating was tested (as described in Example 1) over 8 times more CuO was accessible by hydrogen than by ethane.

#### COMPARATIVE EXAMPLE 1

##### Testing of Uncoated Cu/Silica

The uncoated Cu/SiO<sub>2</sub> was tested using the method described in Example 1. The hydrogen uptake was 22ml and the CO<sub>2</sub> production was 6.6ml. Equal amounts of CuO were accessed by H<sub>2</sub> and ethane.

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**COMPARATIVE EXAMPLE 2****Preparation of Zeolite 4A-Coated Sample Without Using Polyelectrolyte**

A sample of Cu/silica was coated with zeolite as described in Example 1, without first treating it with the polyelectrolyte. When the coating of this sample was tested, only 3 times more CuO was accessed by  $H_2$  than by ethane.

**Claims**

1. A method for the deposition of a coating of a synthetic zeolite onto a substrate material, comprising the treatment of the material with a polyelectrolyte prior to or simultaneously with formation of the zeolite in an alkaline reaction medium surrounding the material.
2. A method according to claim 1, wherein the zeolite is a Na-4A zeolite.
3. A method according to claim 2, wherein the zeolite is modified *in situ* after deposition, by ion exchange.
4. A method according to claim 3, wherein the zeolite is modified by ion exchange with a Group I metal.
5. A method according to claim 4, wherein a Na-4A zeolite is modified to at least partially become a K-3A zeolite.
6. A method according to any one of claims 1 to 5, wherein the polyelectrolyte is a polyacrylamide or a homopolymer of dialyl and dimethyl ammonium chloride.
7. A method according to any one of the preceding claims, wherein the medium for zeolite formation is at pH 10 to 11.
8. A method according to any one of the preceding claims, wherein the material is a catalyst.
9. A method according to claim 8, wherein the catalyst also acts as a hydrogen storage material.
10. A method according to claim 9, wherein the catalyst comprises copper oxide deposited on an oxidic support.
11. A method according to any one of claims 1 to 7, wherein the material is a metal membrane or sheet, or a metal oxide particle.
12. A method according to any one of the preceding

claims, comprising the step of autoclaving the coated material.

13. A method according to any one of the preceding claims, comprising calcination.
14. A method according to any one of the preceding claims, comprising the step of depositing a second coating.
15. A copper catalyst deposited on an oxidic support and having a substantially complete coating of a zeolite.
16. A catalyst according to claim 15, wherein the zeolite is a 3A or 4A zeolite.
17. The use of a catalyst prepared by a method according to any one of claims 1 to 14, or according to claim 15 or 16, in a catalytic chemical process involving the storage of hydrogen.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 3083

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (INCL.6)
D,Y	WO 94 05608 A (BP CHEM INT LTD) 17 March 1994 * claims 14-17; example 2 *	1-14	B01J25/00 B01J25/72 B01D71/02 C01B3/00
Y	WO 95 33561 A (AKZO NOBEL NV ;MOUTERT FRANCISCUS WILHELMUS V (NL); BRUIJL HENDRIK) 14 December 1995 * page 12, line 12 - page 13, line 7 *	1-14	
Y	US 5 316 656 A (PELLET REGIS J ET AL) 31 May 1994 * column 6, line 42 - column 8, line 26; claim 1 *	1-14	
A	WO 96 01686 A (EXXON RESEARCH ENGINEERING CO) 25 January 1996 * page 18, paragraph 2; claims 1-12 *	1-14	
			TECHNICAL FIELDS SEARCHED (INCL.6)
			B01J B01D C01B
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 19 August 1998	Examiner Schwaller, J-M
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: prior art document X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: supplementary finding round D: non-patent literature P: prior art document	

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European Patent  
OfficeLACK OF UNITY OF INVENTION  
SHEET B

Application Number

EP 98 30 3083

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

## 1. Claims: 1-14 and 17

A method for the deposition of a coating of a synthetic zeolite onto a substrate material, comprising the treatment of the material with a polyelectrolyte prior to or simultaneously with formation of the zeolite in an alkaline medium surrounding the material and use thereof in a catalytic chemical process involving the storage of hydrogen

## 2. Claims: 15-17

a copper catalyst deposited on an oxidic support and having a substantially complete coating of a zeolite and its use in a catalytic chemical process involving the storage of hydrogen.